Growth of Epitaxial Potassium Niobate Thick Films by Hydrothermal Method and Their Electrical and Ferroelectrical Properties

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ABSTRACT

Epitaxially-grown $KNbO_3$ thick films over 10 μm in thickness were successfully obtained at 240 °C for 3 h on (100)$SrRuO_3$//$SrTiO_3$ substrates by a hydrothermal method. Crystal structures were systematically investigated for the epitaxial $KNbO_3$ films as well as the ferroelectric and piezoelectric properties. Additionally, epitaxial $SrRuO_3$ layers grown on (100)$SrTiO_3$ substrates by sputter method were used as bottom electrode layers. Relative dielectric constant and the dielectric loss were 415 and 0.08, respectively. Clear hysteresis loops originated from the ferroelectricity were observed and a remanent polarization was 20 μC/cm^2 at a maximum applied electric field of 196 kV/cm.

INTRODUCTION

Recently, Piezoelectric and ferroelectric materials are utilized for micro actuators, ultrasonic transducer and memory devise in medical area. Therefore lead-free piezoelectric materials have been widely investigated for the requirement of the exclusion of the toxic element such as lead, which is essential one for the present high performance piezoelectric materials, for example PZT. $KNbO_3$ [1], $KNbO_3$-based and related materials, such as (K, Na)NbO_3 [2] and (1−x)($K_{0.5}Na_{0.5}$)NbO_3 − x$LiNbO_3$ [3], have been widely investigated. Films of $KNbO_3$ or $KNbO_3$-based materials have been reported by several methods [4-6], however the difficulty of the K/Nb ratio control was pointed out due to the high volatility of potassium, especially for the deposition methods operated under vacuum condition.

Hydrothermal method is a unique method for growing the ferroelectric materials because the films were grown under high pressure instead of the widely investigated low pressure and crystalline films were grown at relatively low temperature [7]. In addition, excellent conformability is expected due to their inhomogeneous nucleation on the substrate surface, which results in the conformal growth even on the surface with complex shape. However, the electrical property of the hydrothermally

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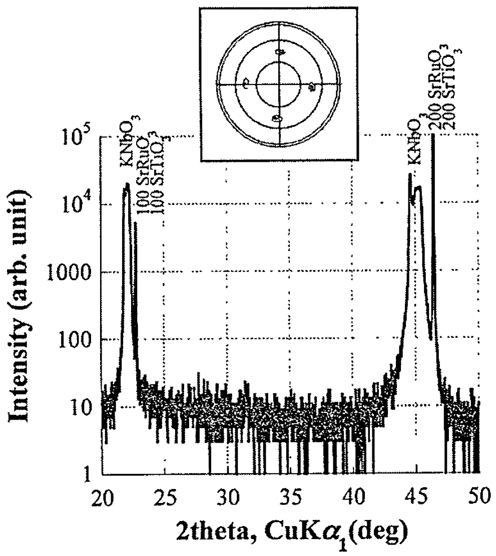

Fig.1 XRD pattern of $KNbO_3$ film deposited on $(100)_cSrRuO_3//SrTiO_3$ substrate together with the X-ray pole figure measurement fixed at 2θ of 31.5°.

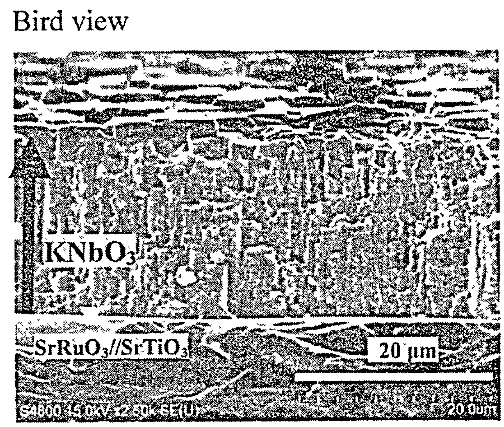

Fig.2 Cross-sectional SEM image of epitaxial $KNbO_3$ film deposited on $(100)_cSrRuO_3//$ $SrTiO_3$ substrate.

grown $KNbO_3$ films has been hardly reported, even though their epitaxial films were reported [8-13] In the present study, epitaxial $KNbO_3$ films were grown on $(100)SrRuO_3//(100)SrTiO_3$ substrates and the ferroelectric properties were ascertained for the first time. Moreover, the transmitting and receiving of ultrasonic waves over 60MHz using epitaxial $KNbO_3$ films were demonstrated.

EXPERIMENTAL PROCEDURE

The $KNbO_3$ thick films were grown on the (100) $SrRrO_3//$ $(100)SrTiO_3$ substrates at the deposition temperature of 240 °C by the hydrothermal method. Epitaxial (100)-oriented $SrRuO_3$ layers were grown on $(100)SrTiO_3$ substrates by sputtering methods and were used for the bottom electrodes, $(100)SrRrO_3//$ $(100)SrTiO_3$ [14] .

The 10 *ml* solution of potassium hydroxide (KOH, Kantoukagaku Co., Ltd.) and 1.0 g powders of niobium oxide (Nb_2O_5, purity 99.9%, Kantounkagaku Co., Ltd.) were put in an autoclave (PARR, 4748) as the source materials together with the (100)c $SrRrO_3//SrTiO_3$ substrates. The autoclave was closed to retain water vapor and was placed in a constant-temperature oven for the hydrothermally chemical reaction for 3 h.

The film composition was measured with X-ray fluorescence spectroscopy (XRF, HORIBA, 7593H). The thickness of the obtained film was determined by a scanning electron microscopy (SEM, HITACH S-4800) and their crystal structure was characterized with high resolution X-ray diffraction (HRXRD, Philips X'Pert MRD system) analysis using a four-axis diffractometer with Cu $K\alpha_1$ radiation. The electrical properties were measured at room temperature as $Pt/KNbO_3/$ $SrRuO_3$ capacitors after making platinum top electrodes with 100 μm in diameter, which were deposited by the electric beam evaporation.

RESULTS AND DISCUSSIONS

The K/Nb ratio of the obtained films was evaluated to be 51/49, suggesting that the films with almost stoichiometric composition were obtained in the present condition. X-ray θ - 2θ pattern is shown in Fig. 1 for the $KNbO_3$ film

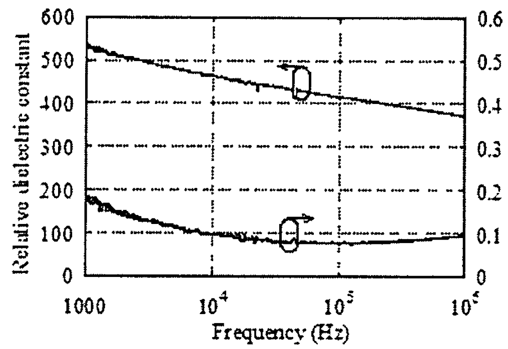

Fig.3 Frequency dependence of the relative dielectric constant and the dielectric loss.

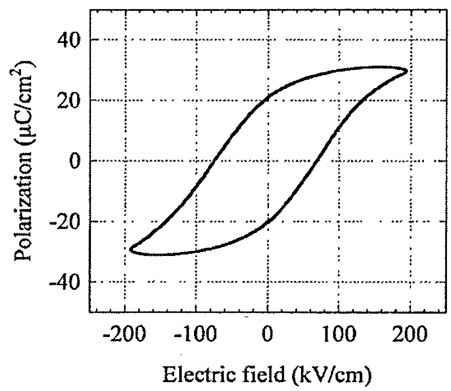

Fig.4 *P–E* hysteresis loops measured at 100 kHz and maximum applied electric field of 196 kV/cm.

grown on $(100)_c$ $SrRrO_3$//$SrTiO_3$ substrate. Two sprit peaks were observed at around 22 ° and 45 ° together with those from the substrate. The lattice constants calculated from each sprit peaks were found to be approximately 4.06 Å and 4.00 Å. The reported data [15,16] suggest that the lattice parameters of (100)/(001) tetragonal $KNbO_3$ are 4.062 Å/3.993 Å, while those of (100)/(110) orthorhombic $KNbO_3$ with pseudo cubic unit cell are 4.036 Å/3.974 Å, respectively. The detail crystal structure analysis of the obtained film is under investigated because the lattice parameters of the obtained films are possible to be strained by the clamping force from the substrate.

X-ray pole figure measured at a fixed 2θ angle at 31.5° is inserted in Fig.1, corresponding to the tetragonal {110} or orthorhombic {111}. It had a four fold symmetry at inclination angle of about 45°. This suggests the cube-on-cube epitaxial growth of this film.

Figure 2 shows a cross-sectional SEM image of the same $KNbO_3$ film whose x-ray profile is shown in Fig.1. Relatively dense film with large thickness was ascertained to be grown on $(100)_c$ $SrRrO_3$// $SrTiO_3$ substrate. Figure 3 shows the frequency dependency of the relative dielectric constant, ε_r, and the dielectric loss of the Pt/$KNbO_3$/ $SrRrO_3$/ capacitor. The ε_r and the dielectric loss at 100 kHz were 416 and 0.08, respectively. The $P-E$ relationships measured at 100 kHz at room temperature is shown in Fig. 4 for the Pt/$KNbO_3$/$SrRrO_3$/ capacitor. Clear hysteresis loops originated from their ferroelectricity were observed for the first time as the hydrothermally - grown epitaxial thick film, even though the contribution from the leakage was not perfectly negligible. Observed remanent polarization, P_r, was 20μC/cm^2 at the maximum electric field of 196 kV/cm and this P_r value was almost the similar to the reported one for the sintered body [17]. The results shown in Fig.4 indicated that the present $KNbO_3$ film is able to drive for the high power operation.

CONCLUSIONS

The epitaxially-grown $KNbO_3$ thick films over 10 μm in thickness were successfully obtained on the (100)$SrRuO_3$//$SrTiO_3$ substrates at 240 °C for 3h by the hydrothermal method. The dielectric constant ε_r and dielectric loss were 416 and 0.08, respectively. The clear hysteresis loops originated from the ferroelectricity was observed and the P_r was 20 μC/cm^2 at the maximum applied electric field of 196 kV/cm.

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